

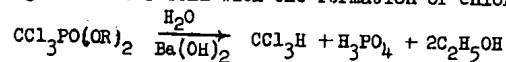
S-E-C-R-E-T

50X1-HUM

This neutral ester can be obtained by the reaction $\text{CCl}_3\text{PCl}_4 + 4\text{C}_2\text{H}_5\text{ONO} \rightarrow \text{CCl}_3\text{PO}(\text{OC}_2\text{H}_5)_2 + 4\text{NOCl} + (\text{C}_2\text{H}_5)_2\text{O}$.

The diethyl ester was originally described by Kamay (1).

With the purpose of getting trichlorophosphonic acid, the saponification of its esters under various conditions was studied. It developed that in an alkaline medium (barium hydroxide) the diethyl ester of trichloromethylphosphonic acid undergoes splitting at the C-P bond with the formation of chloroform:



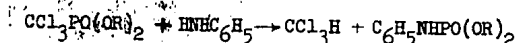
Saponification of the ester in cold 15% HCl results in the formation of the above-described acid ester $\text{CCl}_3\text{PO}(\text{OC}_2\text{H}_5)\text{OH}$, even though the saponification may have been carried out for a very long time (2-3 months).

Free trichloromethylphosphonic acid (in the monohydrate form) forms in practically quantitative yields during the saponification of its esters in 15% HCl at 140-150° for 3-4 hr.

According to Kamay's data, the initial acid cannot be obtained by saponification of the esters of trichloromethylphosphonic acids. The reaction allegedly is accompanied by a full decomposition of the ester and the formation of phosphoric acid. These assertions, according to our data, are erroneous.

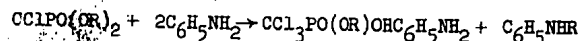
Trichloromethylphosphonic acid is dibasic. Silver nitrate precipitates its disilver salt, which dissolves with difficulty in water. This salt decomposes explosively under light heating. On treating the acid with diazoaliphatic compounds, the corresponding esters are obtained.

In accordance with Kamay's data, trichloromethylphosphonates react with aniline as follows:



We were unable to substantiate this. The methyl and ethyl esters of trichloromethylphosphonic acids behaved alike when heated with aniline in boiling toluene, forming aniline salts of acid esters of trichloromethylphosphonic acid.

Thus the reaction seems to consist of the alkylation of aniline as follows:



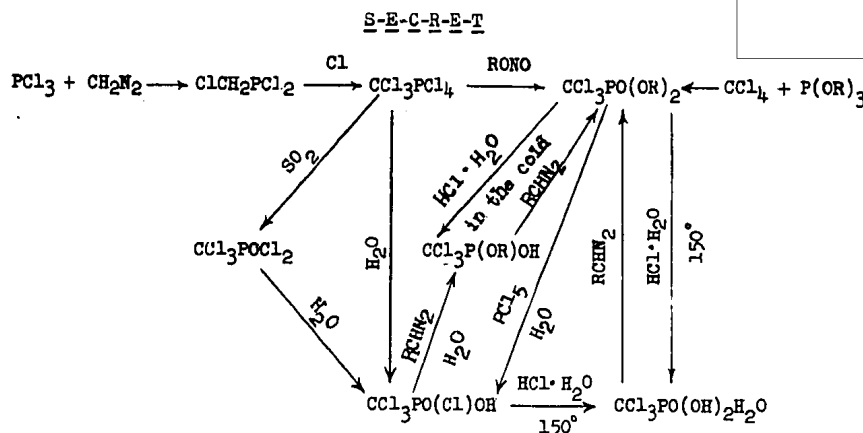
Experimental data seem to refute Todd and Atherton's scheme for this reaction (3).

In order to establish relationship between $\text{CCl}_3\text{PO}(\text{OH})_2$ and $\text{CCl}_3\text{PO}(\text{Cl})\text{OH}$, the conditions of their mutual transformation were found. Thus trichloromethylphosphonic acid monochloride, after being heated in a sealed tube with HCl, becomes trichloromethylphosphonic acid. Treating the acid $\text{CCl}_3\text{PO}(\text{OH})_2$ with an excess of PCl_5 or SOCl_2 does not result in the expected acid chloride. Heating the ester $\text{CCl}_3\text{PO}(\text{OR})_2$ with the corresponding amount of PCl_5 at 150° changes the ester into acid /di/ chloride, which, after hydrolysis, yields trichloromethylphosphonic acid monochloride. Some of the reactions of trichloromethyl derivatives of phosphorus can be graphically illustrated as follows:

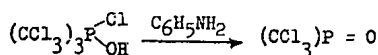
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S-E-C-R-E-T

50X1-HUM



From other trichloromethyl derivatives of phosphorus we obtained derivatives of tri (trichloromethyl) phosphine. Thus, by treating tri (chloromethyl) phosphine with phosphorus pentachloride we obtained the perchloride $(CCl_3)_3PCl_2$. This substance, after boiling in alkali hydroxide, splits off at least one atom of chlorine and becomes the oxychloride $(CCl_3)_3P(Cl)OH$. Treatment of the latter in solution with aniline removes HCl :



Thus, introduction of the trichloromethyl group at the phosphorus atom results in a number of peculiarities in the behavior of this type of organophosphorus compounds. The most important ones are:

1. Sharp decrease in the reactive capacity of the chlorine atom attached to the phosphorus in respect to hydrolysis and ammonolysis.
2. Appearance of a specific reactive capacity of the $C - P$ bond with respect to alkalis, as illustrated by the fact that the $CCl_3 - P$ group behaves like the $CCl_3 - C$ or $CCl_3 - Si$ groups, which in many cases are capable of splitting off chloroform easily under the action of a strong base.
3. The introduction of halogenin, to the methyl group intensifies the acidic properties, so that trichloromethylphosphonic acid is free to form the dianiline salt.
4. The presence of the CCl_3 group next to the phosphorus atom contributes to the stability of the unusual $P \begin{matrix} OH \\ | \\ Cl \end{matrix}$ group.

The listed features point to a similarity in chemical behavior of trichloromethylphosphonic derivatives and compounds of the type of Boyd's acid chloride(4, 5).

Table 1. Properties of the Obtained Organophosphorus Compounds

Compound	Melting Pt	Bp	Density	n_D^{20}
$CHCl_2PCl_4$	Decomposes	--	--	--
$CHCl_2PO(OH)_2$	54	--	--	--
$CHClBrPO(OH)_2 \cdot 2C_6H_5NH_2$	180-185 decomposes	--	--	--

S-E-C-R-E-T

S-E-C-R-E-T

50X1-HUM

<u>Compound</u>	<u>Melting Pt</u>	<u>Bp</u>	<u>Density</u>	<u>n_D²⁰</u>
CCl_3PCl_4	125, decomposes	--	--	--
$\text{CCl}_3\text{POCl}_2$	155	--	--	--
$\text{CCl}_3\text{PO}(\text{OCH}_3)_2^*$	37	109-109.5/9 mm	$d_0^{50} = 1.4830$	1.4620
$\text{CCl}_3\text{PO}(\text{OC}_2\text{H}_5)_2^{**}$	--	122-123/13 mm	$d_0^{14} = 1.3710$	1.4620
$\text{CCl}_3\text{PO}(\text{OH})_2 \cdot \text{H}_2\text{O}$	87	--	--	--
$\text{CCl}_3\text{PO}(\text{OH})_2 \cdot \text{C}_6\text{H}_5\text{NH}_2$	Above 220	--	--	--
$\text{CCl}_3\text{PO}(\text{OH})_2 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$	Above 220	--	--	--
$\text{CCl}_3\text{PO}(\text{OAg})_2$	Explodes	--	--	--
$\text{CCl}_3\text{PO}(\text{Cl})\text{NHC}_6\text{H}_5$	113	--	--	--
$\text{CCl}_3\text{PO}(\text{NHC}_6\text{H}_5)_2$	172	--	--	--
$\text{CCl}_3\text{PO}(\text{OC}_2\text{H}_5)_2 \cdot \text{OH} \cdot \text{C}_6\text{H}_5\text{NH}_2$	176, decomposes	--	--	--
$\text{CCl}_3\text{PO}(\text{OCH}_3)_2 \cdot \text{OH} \cdot \text{C}_6\text{H}_5\text{NH}_2$	172, decomposes	--	--	--
$\text{CCl}_3\text{PO}(\text{Cl})\text{OH}$	79	--	--	--
$\text{CCl}_3\text{PO}(\text{Cl})\text{OH} \cdot \text{C}_6\text{H}_5\text{NH}_2$	191, decomposes	--	--	--
$(\text{CCl}_3)_3\text{PCl}_2$	190, decomposes	--	--	--
$(\text{CCl}_3)_3\text{P}(\text{Cl})\text{OH}$	203	--	--	--
$(\text{CCl}_3)_3\text{P} = \text{O}$	53	--	--	--

*Described by Kamay as a liquid boiling at $121^\circ/12$ mm; $d_0^{15} = 1.4594$; $n_D^{14} = 1.4580$

**Described by Kamay as boiling at $122-123^\circ/12$ mm; $d_0^{14} = 1.3664$; $n_D^{14} = 1.4585$

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